Topic B – Part 4

Lipids ☺

IB Chemistry

Topic B – Biochem

B4 Lipids - 3.5 hours

- B.4.1 Compare the composition of the three types of lipids found in the human body. (3)
- B.4.2 Outline the difference between HDL and LDL cholesterol and outline its importance. (2)
- B.4.3 Describe the difference in structure between saturated and unsaturated fatty acids. (2)
- B.4.4 Compare the structures of the two essential fatty acids linoleic (omega–6 fatty acid) and linolenic (omega–3 fatty acid) and state their importance. (3)
- B.4.5 Define the term iodine number and calculate the number of C=C double bonds in an unsaturated fat/oil using addition reactions. (2)
- B.4.6 Describe the condensation of glycerol and three fatty acid molecules to make a triglyceride. (2)
- B.4.7 Describe the enzyme-catalyzed hydrolysis of triglycerides during digestion. (2)
- B.4.8 Explain the higher energy value of fats as compared to carbohydrates. (3)
- B.4.9 Describe the important roles of lipids in the body and the negative effects that they can have on health. (2)

B4.1 - Lipids

- *B.4.1 Compare the composition of the three types of lipids found in the human body.*
- **Lipids** are a group of substances that contain the elements carbon, hydrogen and oxygen (just as proteins and carbohydrates), but the proportion of oxygen is less than carbohydrates.
- Lipids are **insoluble** in water BUT dissolve in organic solvents
- Occur in living organisms as **triglycerides** (fats and oils), **phospholipids**, and **steroids**.

B4.1 - Triglycerides

- Fats and oils are **triglycerides** that are formed by condensation reactions of propane-1,2,3-triol (**glycerol**) and **fatty acids** (long-chain carboxylic acids).
- The fatty acid chains can be classified as **saturated** (hydrated) or **unsaturated** (kink or double bond)
- Triglycerides are the commonest lipids in living organisms
- At 20°C classified as fats or oils
  - Solid = fats
  - Liquid = oil

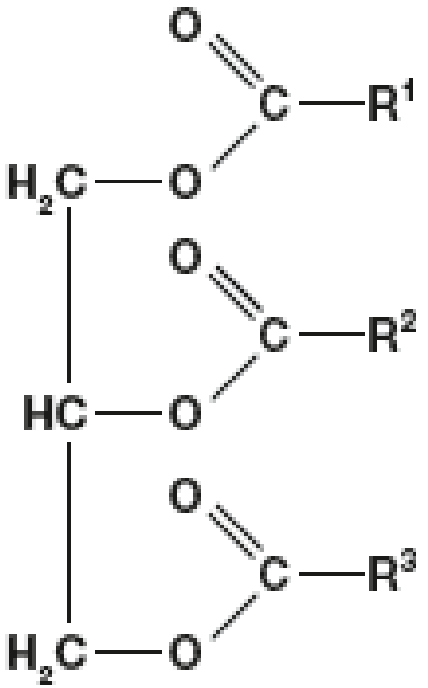


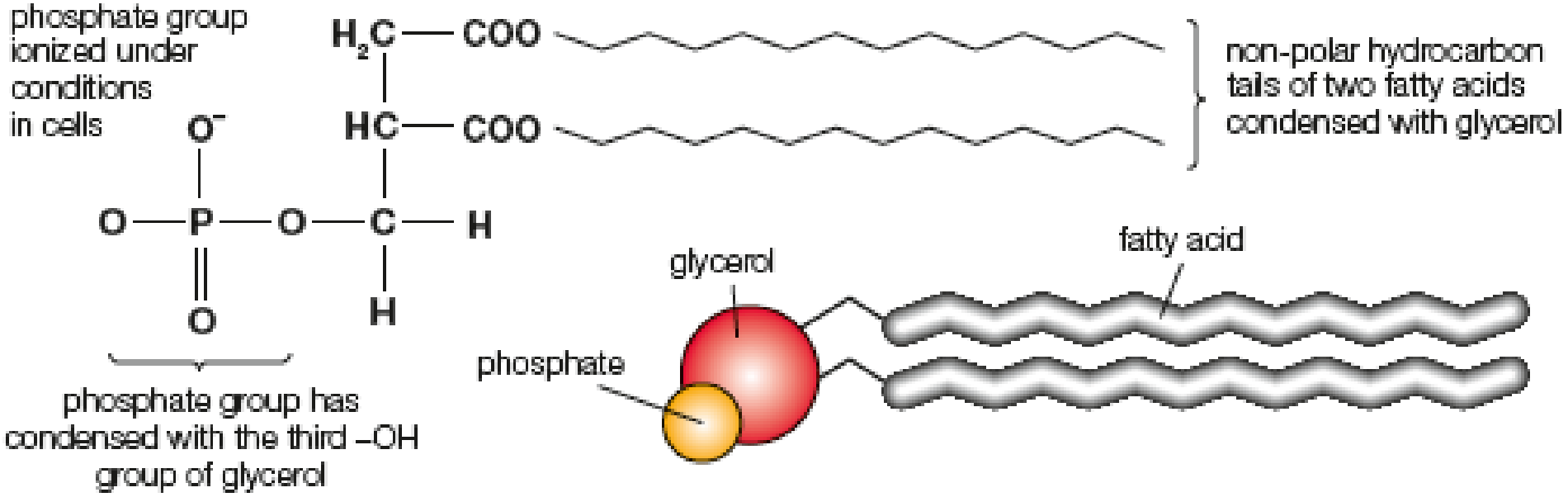
Figure 22.45 The generalized formula of a triglyceride, where R^1, R^2 and R^3 represent fatty acid chains, which may be the same or different

B4.1 - Phospholipids

- **Phospholipids** are similar in structure to triglycerides BUT one of the fatty acid groups is replaced with a **phosphate group**, and are hence known as **diglycerides**.
- The phosphate group is ionized and negatively charged, therefore water molecules are attracted to this **polar part of the molecule**, this end is then **hydrophilic** and soluble in water.
- The two fatty acid chains are **insoluble and nonpolar**

B4.1 – Phospholipids (2)

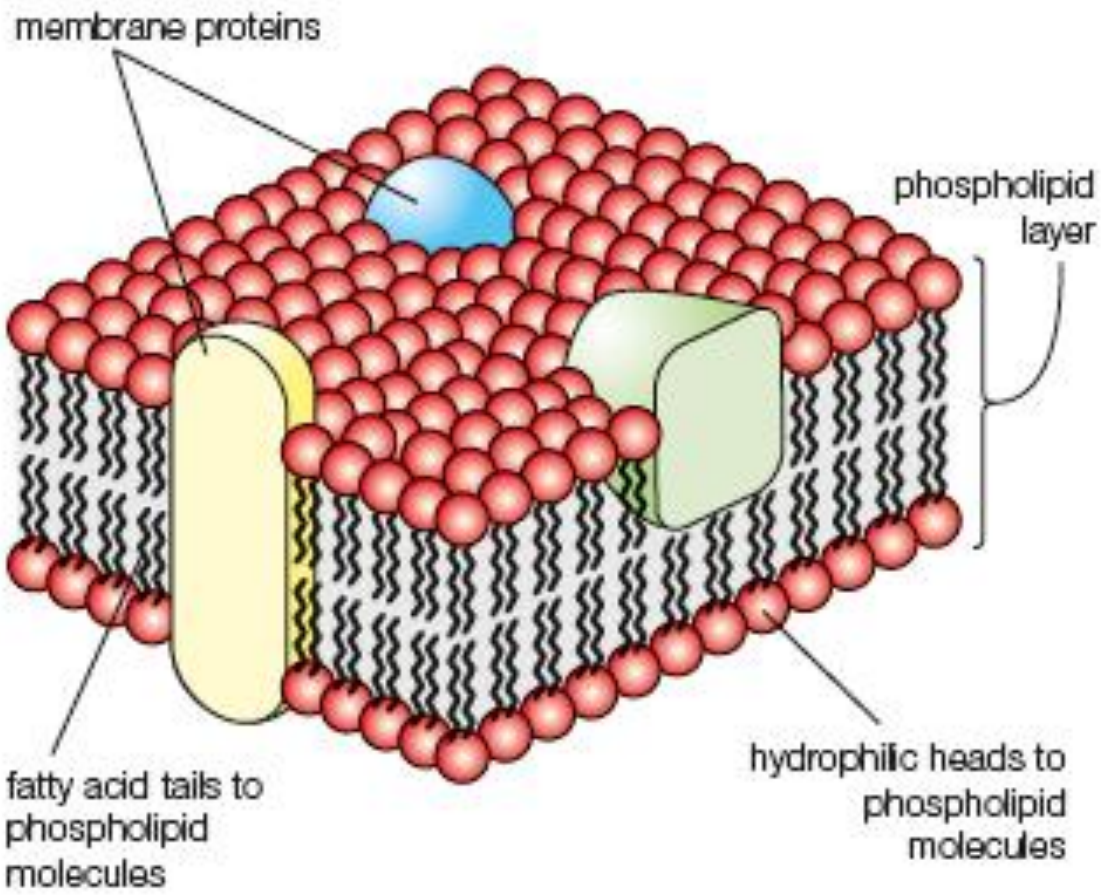
- In cells, these phopholipids occur with proteins and cholesterol in a **bilayer** in the form of a **cell membrane.**
- Bilayers occur when the hydrophobic tails line up with one another with the hydrophilic heads exposed



B4.1 – Phospholipids (3)

- Below is Lecithin, or phosphatidycholine, a major component of biological membranes and can be isolated from egg yolk or soybeans

Focus on the "tails" and "heads" which form a membrane



B4.1 - Steroids

- **Steroids** do NOT contain fatty acids but are still considered to be lipids, this is because they have similar properties to triglycerides and are synthesized using common intermediates.
- Steroids all contain a **17-carbon atom skeleton** that varies due to the functional groups and their oxidation states

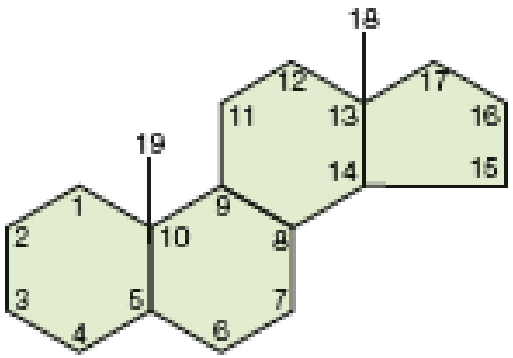


Figure 22.49 The steroid 'nucleus'

B4.1 – Steroids (2) as hormones

- The sex hormones are all steroid-based hormones
  - **Progesterone**: female menstrual cycle
  - **Estrogen**: female sex hormones
  - **Testosterone**: male sex hormones
- **Aldosesterone**, which is secreted by the adrenal gland (secrete hormones from stress), is also steroid-based and aids in controlling the concentration of sodium and potassium.
- **Vitamin D** is a steroid-based vitamin

B4.1 – Steroids (3)

- Found in both **plants** and **animals**
- Form bile acids that help to emulsify and solubilize lipids during the digestion process (more later). **Helps you metabolize lipids!**

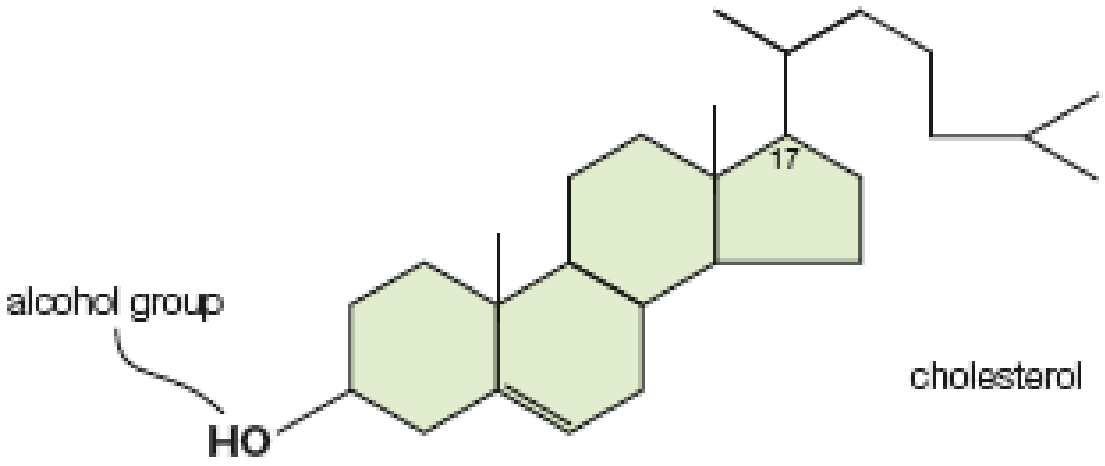


Figure 22.50 The skeletal structure of cholesterol. This is the most abundant steroid in humans

B4.2 - Cholesterol

- *B.4.2 - Outline the difference between HDL and LDL cholesterol and outline its importance*
- **Cholesterol** is found in all tissues as a part of the cell membrane. High concentrations are found in blood, brain, and spinal cord.
- Cholesterol is like other lipids and is insoluble in water (and blood) so is transported in blood plasma within **lipoproteins** known as apoproteins.
- Outer surface of these proteins is polar, and the inner surface non-polar.

B4.2 – Cholesterol (Lipoprotein types)

- There are two main types of Lipoproteins
  - High-density Lipoproteins (**HDL**)
    - Composed of mainly proteins with small amounts of cholesterol
    - Referred to as "good cholesterol" because they help remove cholesterol from artery walls and transport it to the liver for removal from the body
  - Low-density Lipoproteins (**LDL**)"bad cholesterol"
- In healthy individuals, 30% of blood cholesterol is carried by HDL
  - The cholesterol within each is identical

4.2 – Cholesterol LDL

Low-density lipoproteins (LDL) (Figure 22.52) are composed mainly of cholesterol and have very little protein. They are often referred to as 'bad cholesterol' because they are primarily responsible for depositing cholesterol within arteries.

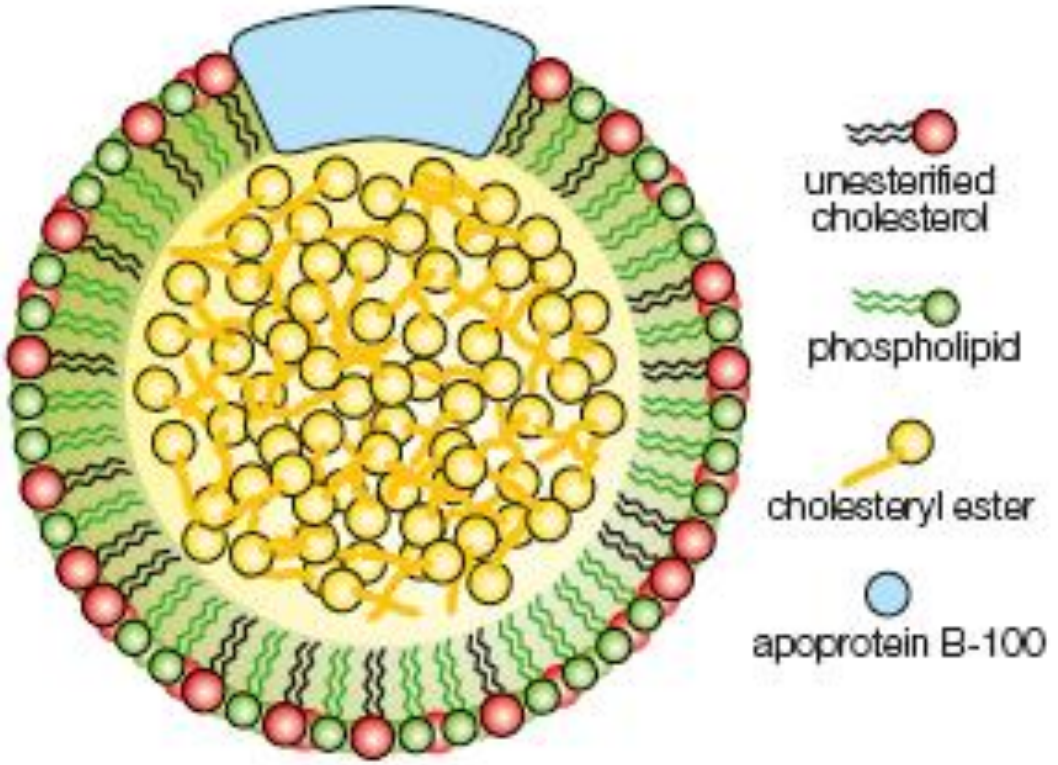


Figure 22.52 Structure of LDL

B4.3 – Structure of Fatty Acids

- *B.4.3. Describe the difference in structure between saturated and unsaturated fatty acids*
- Fats with **unsaturated** fatty acids melt at lower temperatures (oils) than those with **saturated** fatty acids.
- This is a **steric effect** (relevant to shape) because the introduction of a double bond prevents the triglyceride molecules from approaching each other closely and hence interacting via van der Waals' forces.
  - Saturated do NOT react with Br_2 or I_2 (alkane)

B4.3 – Saturated vs Unsaturated

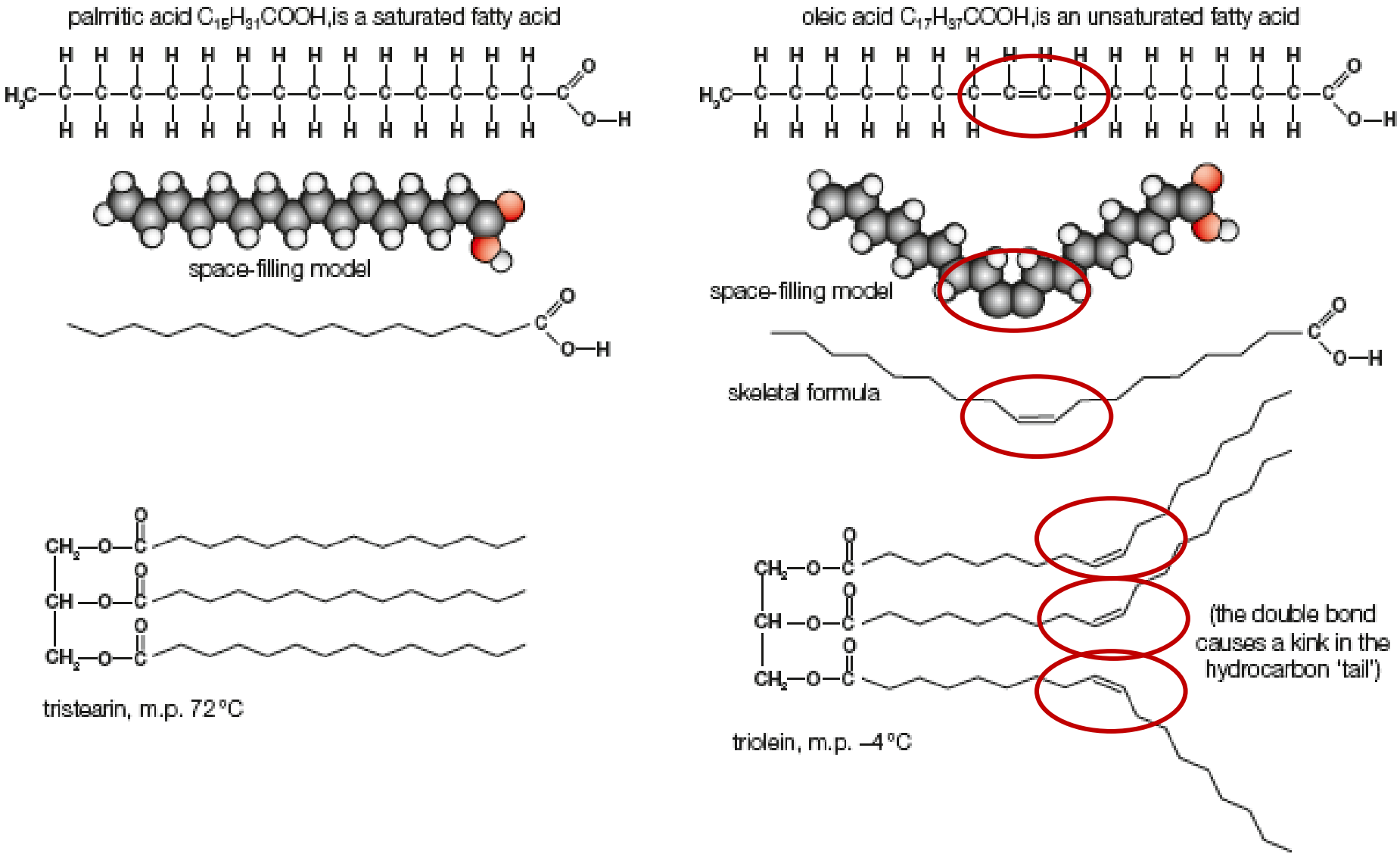
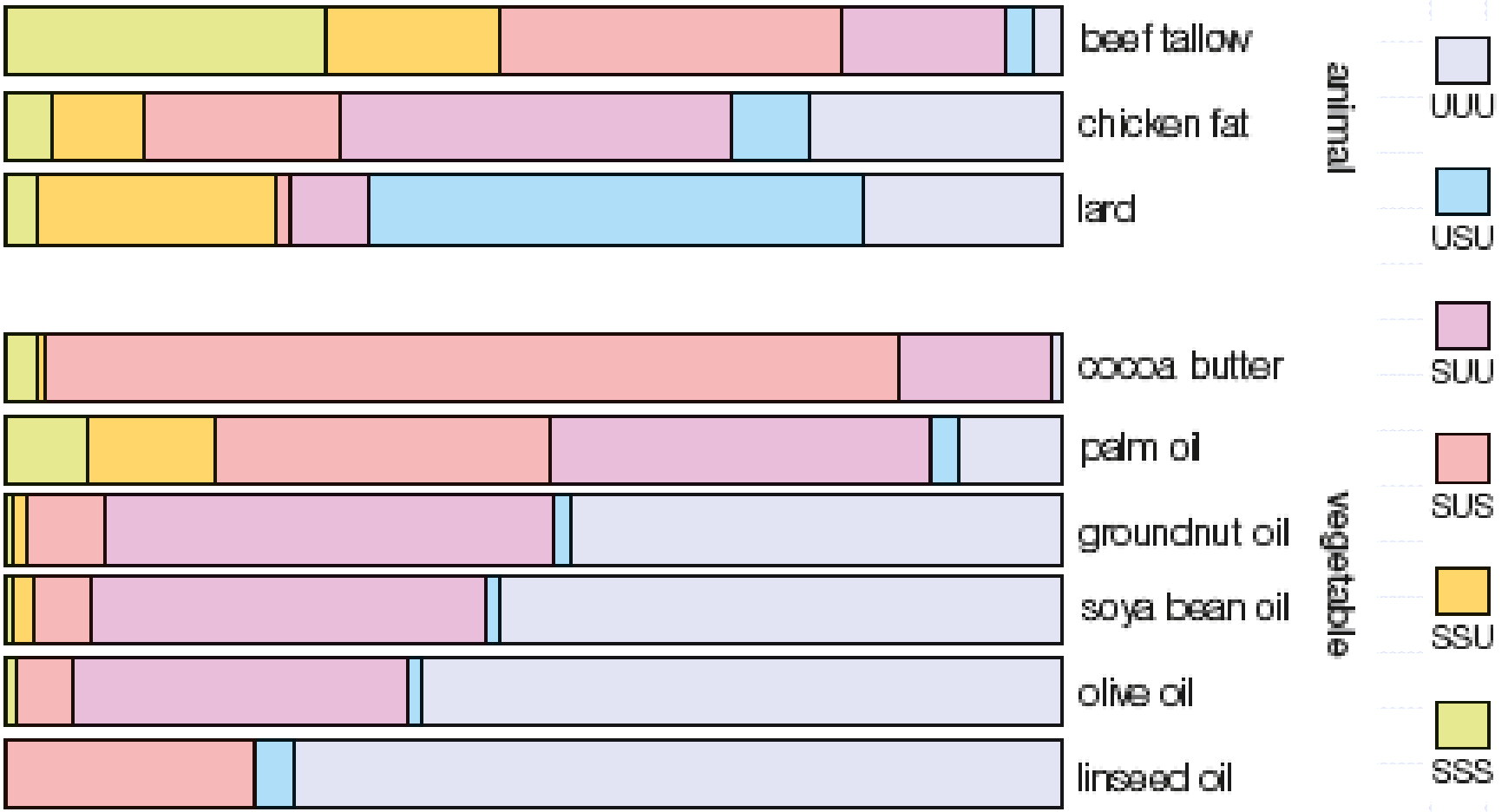


Figure 22.53 Saturated and unsaturated fatty acids, and the triglycerides they form

B4.3 – Saturated v Unsaturated (2)

- Most naturally occurring fats and oils contain a mixture of saturated, mono-unsaturated and poly-unsaturated fatty acids and are classified according to the predominant type in the mixture.
- Linseed soil (flax plant) contains a low percentage of saturated fatty acid residues and is then unsaturated.
- Beef tallow (from beef fat) is high in saturated fat and low in unsaturated fatty acids and is hence saturated.
  - **Animal lipids** are generally **saturated** and **vegetable lipids** tend to be **unsaturated**

B4.3 – Fatty Acid Composition

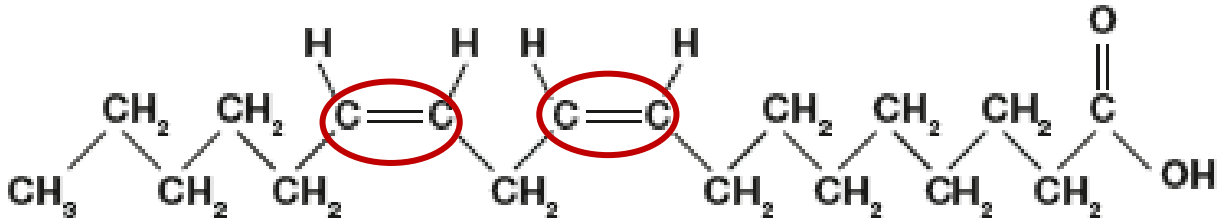


B4.4 – Linoleic and Linolenic acids

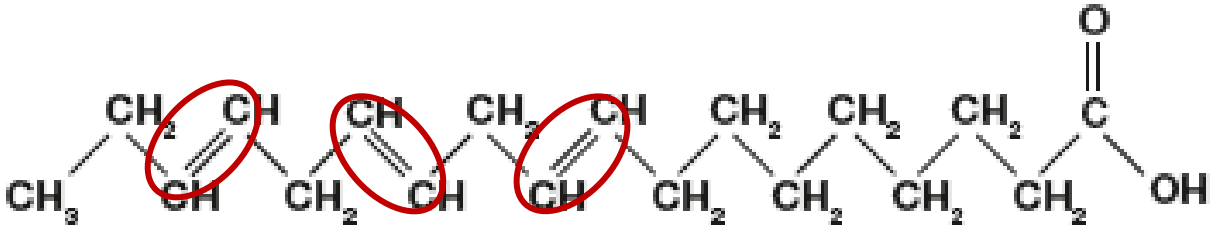
- *B4.4 Compare the structures of the two essential fatty acids in lenoleic (omega-6-fatty acid) and linolenic acid (omega-3-fatty acid) and state their importance*

B4.4 – Linoleic vs Linolenic

- There are two commonly known fatty acid chains
  - **Linoleic** acid (**Omega-6** fatty acids)
    - Carboxylic acid with 18-carbon chain and two cis, C=C, double bonds



  - **Linolenic** acid (**Omega-3** fatty acids)
    - Carboxylic acid with 18-carbon chain and three cis, C=C, double bonds.

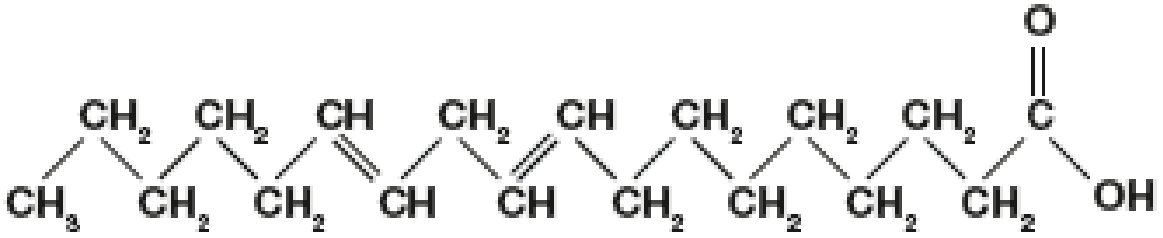


B4.4 – Hydrogenated Oils

- Unsaturated oils can by **hydrogenated** (unsaturated to saturated) to convert them to semi-solid fats
  - Such as margarine which is hydrogenated corn or sunflower oil. These (now more saturated) fats are attractive for backing with a higher melting point and longer shelf life.
  - An **alternative partial process** is often used which has the side effect of producing ***trans*-unsaturated fats** in stead of hydrogenating them completely.

B4.4 – *trans*-unsaturated fats

- *Trans*-unsaturated fats are produced when a partial hydrogenation process is completed.
- Have straight, rather than kinked, shape for the carbon chain, more like the straight chain of a fully saturated fat.



- Margarine contains up to 20% of fatty acids with *trans* double bonds
  - Trans fats increase the amount of LDL in blood, are used like saturated fats BUT block the use of Omega-3 and Omega-6 fatty acids that are vital

B4.4 – *trans*-unsaturated foods

- Foods to be aware of as they often contain unhealthy amounts of *trans*-unsaturated fats
  - Margarine
  - Spreads
  - Cake mixes
  - Fast foods (french frieds, fried chicken)
  - Baked products (biscuits, cakes)
  - Salad dressing
  - Crisps

B4.4 – Linoleic acid Importance

- Research has sown that certain fatty acids are required in the diet. These are known as **essential fatty acids** and cannot be synthesized by the human body
- **Linoleic acid** (Omega-6) is an essential fatty acid and is found in **vegetable oils** such as sunflower oil.
- Linolenic acid (Omega-3) is also very important and can be found in flax seed and fish oil.

B4.5 – Iodine Number

- *B.4.5 Define the term iodine number and calculate the number of C=C double bonds in an unsaturated fat/oil using addition reactions*
- The **iodine number** is the mass of iodine in grams that is consumed by 100 grams of a chemical substance, such as unsaturated lipid.
- Iodine solution is
  - Yellow/brown in color
  - The double bonds will make the color disappear due to the halogen being added across the alkene, but at a precise concentration
  - The amount of I_2 required to keep yellow is the amount of unsaturation in the lipid

B4.5 – Calculating Iodine Number

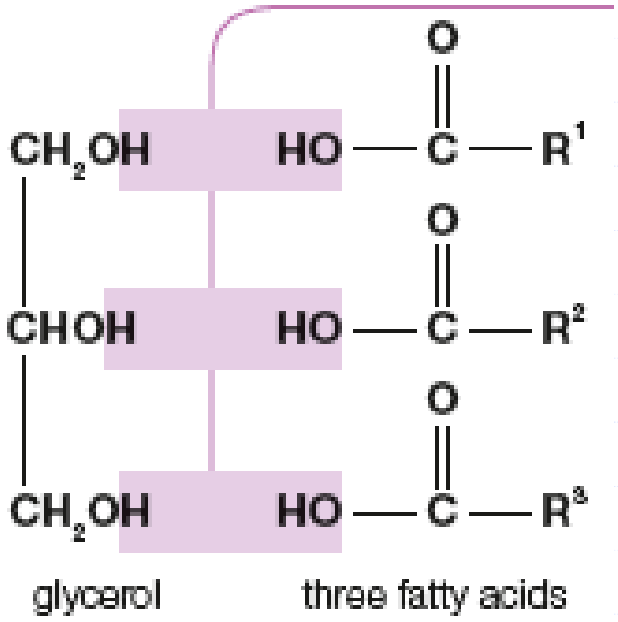
- Determine the number of C=C bonds present in 0.01 moles of linoleic acid when it reacts with 5.10 grams of iodine:
-
- This implies that a ratio of 0.01 mol linoleic acid to 0.0200 mol iodine
- Therefore every molecule of lenoleic acid contains two C=C bonds

B4.5 – Calculating Iodine Number (2)

- Calculate the iodine number of linoleic acid, $C_{17}H_{31}COOH$
- $MM_{linolic\ acid}$ = 280 g/mol
- MM_{iodine} = 254 g/mol
- Linoleic acid has two C=C (from previous calc)
- 280 grams of linoleic acid reacts with 2x254g iodine, hence
- **100g** linoleic acid reacts with —— = 181 g iodine
- Therefore the iodine number of linoleic acid is 181

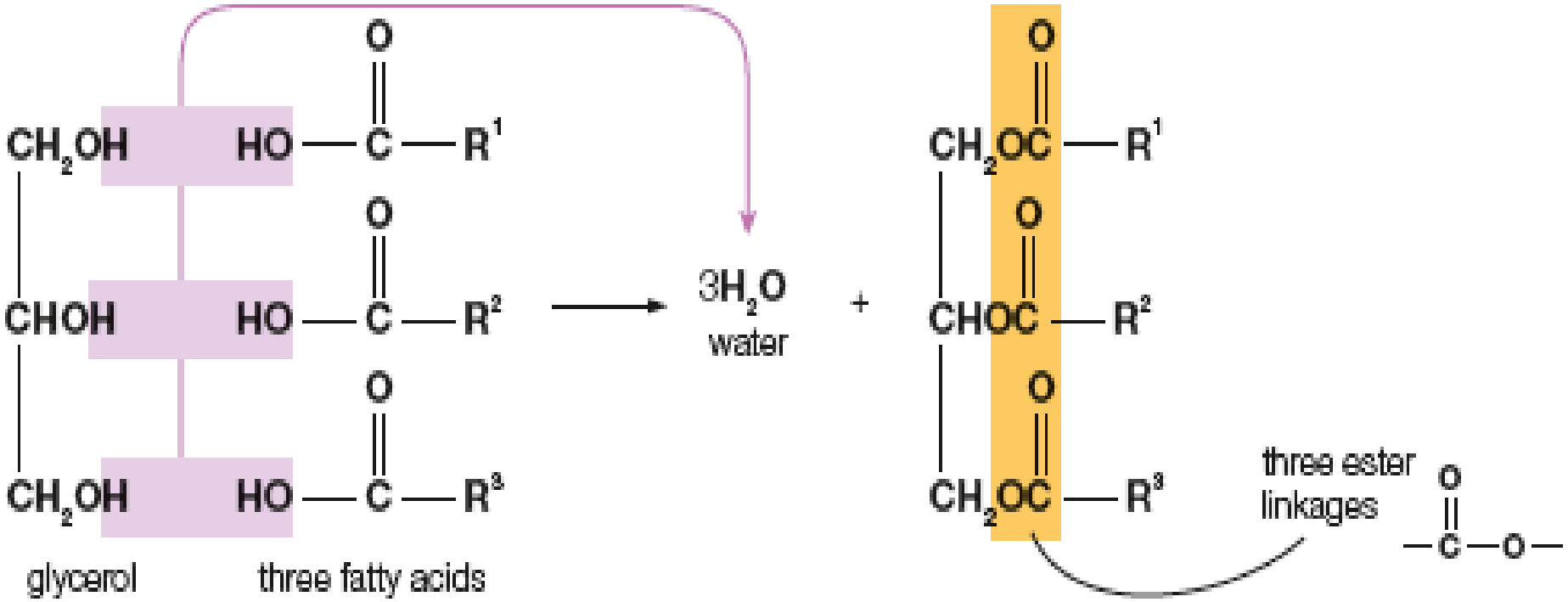
B4.6 – Triglyceride formation

- *B.4.6 Describe the condensation of glycerol and three fatty acid molecules to make a trigylceride*
- **Glycerol** itself has three hydroxyl groups, all of which are able to undergo a **condensation** reaction with a fatty acid molecule to form an ester (esterification).
- Through dehydration synthesis **three water molecules** are thus given off



B4.6 – Triglyceride Condensation

- The fatty acid hydrocarbon chains, R^1, R^2, R^3, may be identical (as in tristearin with three oleic acids.
- However, R^1, R^2, R^3, are generally different



B4.7 – Enzyme-catalyzed hydrolysis

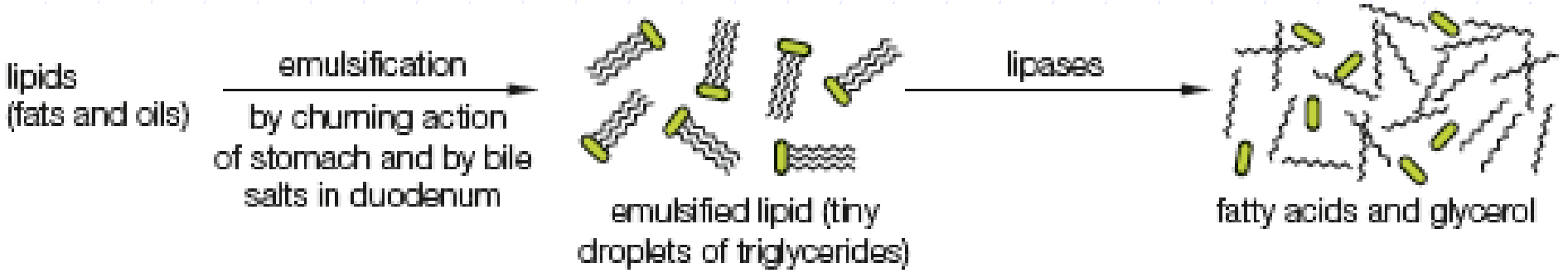
- *B.4.7 Describe the enzyme-catalyzed hydrolysis of glycerol and three fatty acid molecules to make triglycerides*
- **Hydrolysis** is the **opposite** of condensation
- Lipids are **poorly soluble** because of their long nonpolar chains and hence do not undergo significant hydrolysis in water
- **Lipases** are a group of **enzymes directed at lipids** and can break them down chemically
  - Major component of lipids in the human diet is triglycerides

B4.7 – Lipase for Hydrolysis

- In order for lipids to be digested, they must be broken into smaller molecules → Lipase (small amounts in the mouth and stomach) enters the **small intestine** from the pancreas
- Lipase hydrolyzes triglyceride molecules into fatty acid molecules and glycerol molecules.
- Once again, since **lipids are insoluble**, they travel to the small intestine in a congealed mass and **lipase (water soluble) cannot attack the surface**
  - Another material is needed; answer: **Bile**

B4.7 – Lipase + Bile

- To help Lipase attack this congealed mass of tryglycerides, **bile** (produced in the liver but stored in the gallbladder), enters the small intestine via the **bile duct.**
- This **bile emulsifies fats** by dispersing them into small droplets which become **suspended** (not dissolved) in water and lipase can then attack as it has **easier access**.



B4.7 – Products move

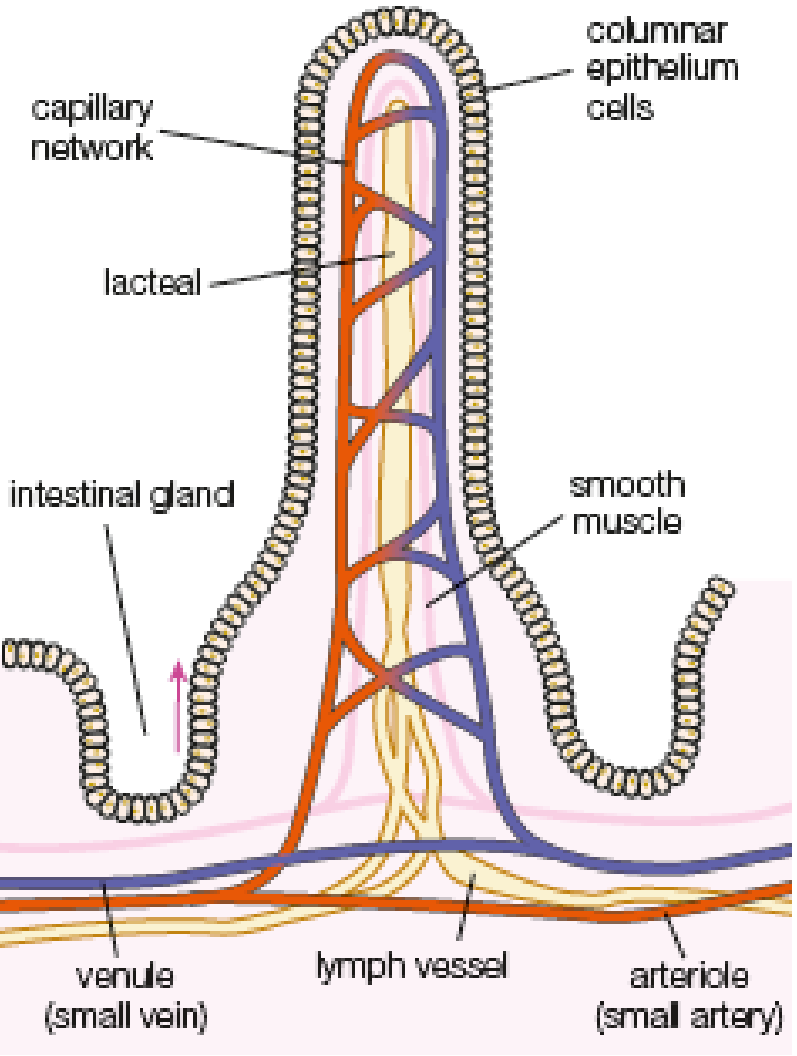


Figure 22.60 The internal structure of a villus in the small intestine

- Absorption of these products (fatty acids and glycerol) occurs in the **villi** (finger like projections which cover the walls of the small intestine).
- The **lymph vessels (lacteals)** absorb both products and drain to the blood stream, transporting triglycerides to the muscle cells for storage or respiration and the glycerol to the liver

B4.8 – Energy value of fats

- *B.4.8 Explain the higher energy value of fats compared to carbohydrates*
- Fats and oils are efficient **long-term stores** of chemical energy.
- Typical fats and oils provide about **38 kJ/g** of energy while typical carbohydrates provide only **17 kJ/g.**
  - This is **due to the composition of lipids** which contain a higher proportion by mass of hydrogen and carbon than sugar.

B4.9 – Role of Lipids in the Body

- *B.4.9 Describe the roles of lipids in the body and the negative effects that they can have on health*
- Major function = long-term energy storage
  - Higher calorific value than carbohydrates
  - Can be respired when glycogen levels in liver and muscles run low
  - Fat is also respired after exercise so that glycogen levels can be restored
- Structural function = insulation
  - For hibernating, heat loss, aquatic mammals
  - Protects organs (kidneys and intestines)

B4.9 – Role of Lipids (2)

- Plants store oils, rather than fats
  - Seeds and fruits are rich in oils
- When fat is respired (oxidized), water is the product
  - This is known as **metabolic water** and is essential to animals that live in hot desserts
  - The **camel stores fat** in their humps, not as an energy source but as a **water source**!

B4.9 – Role of Lipids (3)

- **Phosopholipids** = cell membranes in plant, animal and bacteria cells
- **Lipoproteins** = cell membranes and play important role in the transport of cholesterol in blood
- **Steroids** = both in animals and plants, wide range of functions (precursors to sex hormones and aldosterone, also involved in the synthesis of bile)
- **Omega-3** (linolenic) = found in fish oil, vegetables. Not made by the body, must be consumed, lower bodies production of triglycerides, aids with depression and anxiety

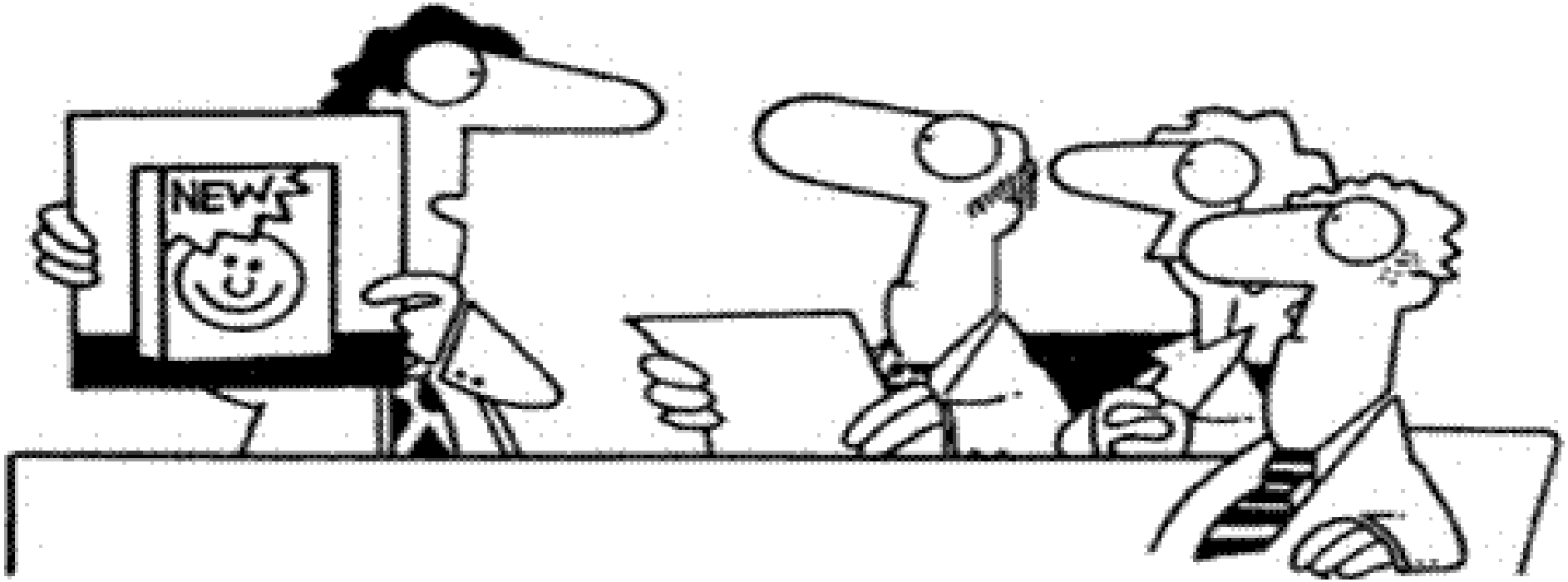
B4.9 – Role of Lipids

- **Mono-unsaturated fat** = primary fat source found in olive oil
  - LDL cholesterol-lowering effect when substituted for equal amounts of saturated fat
  - Reduce risk of heart disease, helps control blood sugar levels
- **Animal fats** = contain saturated fats
  - Raise blood cholesterol levels, increase heart disease risk
- ***Trans* fats** = in meat and dairy products in small amounts, most produced through hydrogenation
  - Solid at room temp, like saturated, raise LDL, decrease HDL cholesterol levels

Fatty Cartoon #1

"Large doses of fish oil are very good for your heart. Especially when you get the urge to swim upstream."

Fatty Cartoon #2



"Our new product has no fat, no cholesterol, no calories, no sugar, no salt and no preservatives. The box is empty but it has exactly what everyone wants!"